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Annual Progress Report

MECHANISM OF VARIOUS ORGANIC REACTIONS

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MECHANISM OF VARIOUS ORGANIC REACTIONS

Analogies are commonly drawn between sulfate and sulfonic esters and the corresponding alkyl halides (1), the attention being focused on the alcohol moiety. Tommila (2,3) and Goubau (4) have made kinetic studies of alcoholysis of aromatic sulfonyl chlorides. Similar kinetic studies of aliphatic sulfonyl chlorides carried out as part of this project (5) have demonstrated the bimolecular nature of the alcoholysis in agreement with the findings of Tommila (2) with aromatic sulfonyl chlorides. Thus an analogy can also be drawn between aliphatic sulfonyl chlorides and primary alkyl chlorides.

In order to determine the steric requirements of various sulfonyl chlorides for comparison with those of the analogous primary alkyl halides it was proposed to study the kinetics of alcoholysis of a selected group of variously branched sulfonyl chlorides. As most of the compounds in this group were unknown a considerable part of the effort toward carrying out this program has been directed toward the preparation of some of them.

Synthesis and properties of the required sulfonyl chlorides has led to study of the mechanism of some of the reactions involved, particularly an explanation of the failure of the retropinacol rearrangement to occur (6) when one might normally have expected it, the mechanism of formation of sulfonyl halides by reacting a Grignard reagent with sulfuryl chloride and the mechanism of decomposition of unstable aliphatic sulfonyl chlorides. Cherbuliez has proposed a one-step reaction for the synthesis (7) while Richter indicates that sulfuryl chloride forms equimolar quantities of sulfinic acid salt and alkyl chloride with Grignard reagents (8). Smook has recently shown that polyethylenesulfonyl chlorides can be decomposed by a free radical mechanism initiated by ultraviolet light (9).

If the sulfo group is considered to be analogous to the methylene group from a mechanistic viewpoint the steric requirements of tertiary sulfonyl chlorides should be considerable, probably enough to force displacement reactions through the higher energy S_N1 mechanism. This seems to be borne out by the fact that the product resulting from reacting sulfuryl chloride with t-butylmagnesium chloride does not form a sulfonamide with an amine but yields t-butyl chloride and the sulfur dioxide addition product of the amine (5). The decomposition of sulfonylium ion to carbonium ion is without parallel for carbonium ions.

Asinger reports the preparation of t-isobutanesulfonyl chloride in good yield from the corresponding sulfonic acid with phosphorus pentachloride (10). By analogy to the conversion of neopentyl alcohol into a halide a rearranged product

would be expected instead of the corresponding sulfonyl chloride or a product resulting from decomposition of the sulfonylium ion might be expected. Asinger's sulfonyl chloride has distinctly different physical and chemical properties from that prepared from the Grignard reagent; the former is a stable liquid which readily yields a sulfonamide whereas the latter is an unstable solid which reacts readily enough with amines but, as pointed out above, does not yield a sulfonamide. Numerous other discrepensies in the t-butyl system also were pointed out in past reports, there being contradictory reports regarding the sulfonic acid and its esters as well as the sulfonyl chloride.

Discussion

Contrary to current views, strained cations do not rearrange per se but are rearranged by base attack at the beta carbon atom. Oxonium ions form little unrearranged products from normal S_N2 attack when this attack is sterically hindered. Instead there occurs an unhindered attack by the carbanion displaced by the base attack at a beta carbon atom. Access of the beta carbon atom to base attack and strength of attacking base determine the proportion of rearranged products. Increasing the steric requirements of the base or the beta carbon atom prevents rearrangement by shielding the beta carbon from attack. Electron-dense substituents can also shield the beta carbon. Attached to this report is a reprint of a publication discussing these views.

In view of the facts that reacting Grignard reagents with sulfuryl chloride results in sulfonyl halide yields generally of the order of some thirty percent and in formation of considerable byproduct alkyl chloride it is believed that the sulfinic acid is an intermediate. If this is correct the halomagnesium salt of the sulfinic acid represents another analogy between the sulfo and the methylene groups and the salt should have some of the properties associated with Grignard reagents. It is probable that the chlorinating action of sulfuryl chloride on the Grignard reagent results in the byproduct alkyl chloride and that analogous chlorination of the halomagnesium sulfinate forms the sulfonyl chloride. By eliminating the possibility of chlorination of Grignard reagent it should be possible to obtain much better yields of sulfonyl chlorides than are generally obtained. As a preliminary step in establishing this mechanism benzylmagnesium chloride was reacted with sulfur dioxide and the product was chlorinated. The yield of a-toluenesulfonyl chloride was about sixty percent and it is expected that a short study of conditions and chlorinating agent should result in considerably more increase over the normal thirty-five percent from reacting the Grignard reagent

directly with sulfuryl chloride. This proposed mechanism for sulfonyl chloride formation rather than a one-step one might account for unsuccessful attempts (11) to prepare sulfonic esters by reacting Grignard reagents with ethyl chlorosulfonate. An unexpected advantage in the change from sulfuryl chloride is that neither step is particularly exothermic whereas the action of sulfuryl chloride is quite violent. Since the decomposition of sulfuryl chloride into sulfur dioxide and chlorine should be endothermic this suggests that the violent action of sulfuryl chloride is due to alkyl chloride formation. A study of heats of reactions involved in sulfonylation of Grignard reagents is now being considered. It is planned to determine the structure of the byproduct alkyl chloride formed in B-strained cases, for example neopentylmagnesium chloride, as it is known that inorganic acid chlorides and aluminum chloride decompose sulfonyl halides into alkyl chlorides (12).

Rates of ethanolysis of sulfonyl chlorides having different steric requirements were determined by refluxing with ethanol containing some hydrogen chloride and finding the amounts of unreacted sulfonyl chloride, of ethyl sulfonate and of sulfonic acid present at various times. Resultant values for the first order solvolytic attack on eight sulfonyl chlorides are summarized:

Sulfonyl chloride	k ($mins.^{-1}$)	$t_{\frac{1}{2}}$ (mins.)
octane-2-	0.014	50
neopentane-	0.016	43
camphane-10-	0.018	39
s-isoamylmethane-	0.048	14
a-toluene-	0.063	11
neopentylmethane-	0.084	8
octane-1-	0.089	8
dl-camphor-10-	0.171	4

From these values it appears that the steric requirements of a sulfonyl chloride having one alpha-methyl group (octane-2-sulfonyl chloride) are of the same order as those of a sulfonyl chloride having two beta-methyl groups (neopentanesulfonyl chloride) or two rigidly fixed beta-methylene groups (camphane-10-sulfonyl chloride). Probably two beta-methylene groups which are not rigidly fixed will increase the steric requirements with consequent retardation of S_N2 attack. On the other hand, two gamma-methyl groups do not appreciably alter the steric requirements for ethanolysis (compare neopentylmethanesulfonyl chloride with octane-1-sulfonyl chloride) but well could slow down attack by a base having considerably greater steric requirements than those of ethanol. One beta-methyl group significantly increases the steric requirements (s-isoamylmethanesulfonyl chloride). These effects are those that

might have been predicted from a comparison of the rates of S_N2 reaction of analogous alkyl bromides (13) when allowance is made for the fact that the sulfur atom is approximately a third larger than carbon.

Although one might expect the phenyl group to participate in the displacement of the chloride from a-toluenesulfonyl chloride by analogy to B-phenyl tosylates (14) the slower rate of ethanolysis ($k = 0.063$ mins.$^{-1}$) compared with octane-1-sulfonyl chloride ($k = 0.089$ mins.$^{-1}$) indicates that this is not the case. The steric requirements of a planar group such as phenyl should be relatively smaller than the bulky ones in camphane-10- or s-isoamylmethanesulfonyl chloride and it is probable that the withdrawl inductive effect of the phenyl group is largely responsible for the slower reaction. Appended to this report is a manuscript submitted for publication concerning steric requirements of sulfonyl chlorides.

The considerably greater rate of ethanolysis of camphor-10-sulfonyl chloride is attributed to the keto group. Very probably its position is critical; in the gamma or in the delta position the carbonyl oxygen should be capable of relatively rapid displacement of the chloride while the ethanol is strongly attracted by the carbonyl carbon. The resultant gamma- or delta-ethoxysultone might be expected to tautomerize to the ethyl gamma- or delta-ketosulfonate if the sulfo group behaves like a carboxyl group. But if the analogy between sulfo and methylene groups is maintained the pseudo-glycosidic structure should not rearrange. In positions closer to the sulfo group a keto group might only have an inductive effect although in the alpha position it might participate through an alpha-sultone intermediate. Conant's studies of the effect of the keto group on rate of reaction of alkyl chlorides with potassium iodide (15) should afford an interesting comparison with its effect on sulfonyl chlorides.

It is planned to further investigate the analogy between alkyl chlorides and sulfonyl chlorides by comparing the neighbor effect in displacement reactions of beta-chloroethyl sulfides (16) and alpha-alkylthiomethanesulfonyl chlorides. Alpha-alkoxymethanesulfonyl chlorides also are of interest in this connection.

Goubau (4) showed that hydrogen chloride catalyzes the ethanolysis of aromatic sulfonyl chlorides. He attributed an apparent drift from first order kinetics to autocatalysis but based his conclusions on total acidity, neglecting to correct for solvolytic attack on the ester, occurring concurrently with attack by hydrogen chloride, which doubles the acidity. The rate of ethanolysis of camphane-10-sulfonyl

chloride was found to be unaffected by as much as a seven-mol ratio of hydrogen chloride to sulfonyl chloride. Some hydrogen chloride was accordingly included in the ethanol used in the alcoholyses in order to reduce the number of variables.

While the reactions of sulfonic esters have been shown to be more nearly like those of alkyl halides (1) the analogy has always been considered from the viewpoint of the alcohol moiety, not the sulfonic acid part. The rates of attack by ethanolic hydrogen chloride and by ethanol on ethyl esters of sulfonic acids having different steric requirements are shown below.

Ethyl sulfonate	k (minutes^{-1})	
	ethanolic HCl	solvolytic
camphane-10-	0.016	0.001
neopentane-	0.029	0.002
s-isoamylmethane-	0.021	0.003
octane-2-	0.041	0.003
neopentylmethane-	0.052	0.003
octane-1-	0.051	0.004

Although these values are not as dependable as those obtained from the sulfonyl chlorides they do show a significant difference in steric requirements. These differences are considerably less than would be expected if the mechanism of reactions of the esters were the same as those of carboxylic esters, in which case they would be about the same as for the sulfonyl chlorides. That solvolysis accounts for only a small part of the attack by the alcoholic hydrogen chloride on the esters is shown by the comparison of rates of attack by ethanol alone. The solvolysis constants are more reliable and are more nearly in agreement with steric requirements. Inconsistences in determinations using ethanolic hydrogen chloride are being studied. An investigation of the steric requirements of sulfonic esters has been initiated in which the sulfonic acid and the alcohol moieties are to be varied. Neutral chloride ion attack seems to be more dependable than hydrogen chloride for this purpose and a comparison of rates and products under the two conditions is being made.

It is believed that t-isobutanesulfonyl chloride is the product obtained from reacting t-butylmagnesium chloride with sulfuryl chloride (5) and not from reacting potassium t-isobutanesulfonate with phosphorus pentachloride (10). The first product is an unstable solid which decomposes slowly to t-butyl chloride and sulfur dioxide and is vigorously decomposed by amines; the second is a stable liquid which reacts with amines as an unhindered sulfonyl chloride. It is believed that the steric requirements of a tertiary sulfonyl chloride are too great for "normal" amine reactions and that the B-strain is so great that instability is characteristic although Folkers (17)

reported a sulfonyl chloride derived from a tertiary sulfonic acid related to penicillamine to form sulfonamides. That Smook found sulfonyl chlorides of polyethylene decompose when irradiated with ultraviolet light (9) does not rule out the possibility of ionic decomposition under normal conditions. If it is requisite for a carbonium ion to assume a configuration approaching planarity a bridgehead carbonium ion in a bicyclo-(2,2,1)-heptane system (18,19) is not possible and a bridgehead sulfonyl chloride of such a system will be stable toward ionic decomposition. Stability of such a sulfonyl chloride will disallow homolytic decomposition since it has been shown that a planar configuration is not requisite to stable free radical formation (20,21).

Chlorosulfonylation of norcamphane might yield three secondary sulfonyl chlorides as well as the tertiary one. Although it is believed that the secondary ones can be preferentially reacted out or decomposed the bridgehead sulfonyl chloride has not yet been isolated. This may be largely because of the very stable emulsions that have been encountered so far. A means of obtaining a bridgehead free radical is a superior route; for example, the brominative decarboxylation of the silver salt of apocamphane-1-carboxylic acid in the presence of sulfur dioxide or sulfuryl chloride is presently being studied. Sulfonylation of a bridgehead carbanion also is being studied.

A third means of obtaining a bridgehead substituent is to form the bridge after the substituent is located. Thus 9,10-dichloroanthracene was reacted with maleic anhydride to yield 9,10-ethanoanthracene-11,12-dicarboxylic acid anhydride. Hydrolysis of the bridgehead chlorides did not occur with aqueous sodium hydroxide below 160°C., at which temperature a retrograde Diels-Alder reaction occurred. Apparently the shorter bond lengths in the aromatic bridges make necessary a greater strain in order to to obtain a bridgehead carbonium ion than in a saturated bicyclo-(2,2,2)-octane system. Attempts to obtain similarly a stable bridgehead sulfur compound have not been successful. During this phase of the investigation 9,10-dichloroanthracene also was reacted with indene. The readily formed adduct, melting at 166°C., apparently is a new compound. Adducts of indene offer the advantage over maleic anhydride of having no funtional groups characteristic of the dieneophile.

Instability of the sulfonyl chloride obtained when t-butylmagnesium chloride is reacted with sulfuryl chloride (5) and failure to obtain a tertiary sulfonyl chloride upon chlorosulfonylating isobutane (10) makes questionable claims to preparing chloro tertiary sulfonyl chlorides by chlorosulfon-

ylating several branched alkyl chlorides (22). No proof of the structures of these supposed tertiary sulfonyl chlorides was presented and the reasoning offered for concluding such structures seems unsound. As a sultone did not result when the acid from hydrolysis of chlorosulfonylated i-butyl chloride was heated under reduced pressure, Helberger concluded that the sulfo group is tertiary on the assumption that the five-membered sultone should have formed if the sulfo group were primary. From this he concluded that the sulfonyl chlorides from chlorosulfonylating each i-amyl chloride and 4-chloro-2-methylpentane must be tertiary since sultones resulted when the acids obtained by hydrolysis of the sulfonyl chlorides were heated under reduced pressure. However if the view is taken that all of the sulfonyl chlorides in question are primary, six-membered sultones formed under the conditions used while the five-membered one did not. This has some support in our failure so far to obtain the five-membered sultone from chlorosulfonylated neopentyl chloride. An investigation is also being made of possible sultone formation from the chlorination product of neopentylmethanesulfonyl chloride, only four or six-membered rings being possible in this case. Attempts to repeat Helberger's work and to prove the structure of his sultones have been initiated.

When diisopropyl was chlorinated in the presence of a 250-watt clear infrared lamp at 20-30°C. the conversion to tertiary chloride was almost twice as great as to the primary while when a 150-watt projector flood lamp was used at 0-10°C. conversion to primary and tertiary was about the same. As this difference may not be fortuitous an investigation is being made, there being no immediately apparent explanation.

New compounds formed in connection with this study are:

S-isopentanesulfonyl chloride, prepared from the sodium salt resulting from addition of sodium bisulfite to B-isoamylene (88% yield, 48% conversion to crude sodium salt) in a dilute alcoholic solution of the nitrate and nitrite of sodium, b. 64-65°/ 1 mm., n_D^{25} 1.4620. The sulfur content was too high for acceptable purity although proportions of the other elements were satisfactory. This new sulfonyl chloride has been derivatized with benzylamine. The amide, m. 86-87°, was not quite analytically acceptable.

Cyclopentanesulfonyl chloride, obtained by chlorosulfonylating cyclopentane, b. 55°/ 0.4 mm., n_D^{25} 1.4889. The sulfur content was too high for analytical purity although the proportions of the other elements were satisfactory. Actually this is not a new sulfonyl chloride but it has not been adequately characterized (23).

Neopentanesulfonyl chloride, previously reported, has been further derivatized with morpholine and with n-butylamine. The amides, each of which are analytically acceptable, melt at 113-114° and 54-55°, respectively. The morpholide of neopentanedisulfonic acid, m. 159-160°, obtained by reacting with morpholine the less volatile residual byproduct from chlorosulfonylation of neopentane, was analytically acceptable.

Chloroneopentanesulfonyl chloride, obtained as a byproduct in chlorosulfonylation of neopentane, b. 78-79°/ 0.8 mm., 84-85°/ 1.8 mm., n_D^{25} 1.4838. The chlorine content was unacceptably low although proportions of the other elements was satisfactory. This sulfonyl chloride was derivatized each with ammonia, benzylamine and morpholine, the melting points of the amides being, respectively, 85-86°, 63-64°, 109-110°. Only the last has been shown to be analytically acceptable material, the second one is almost so, the first has not been analyzed.

Neopentylmethanesulfonyl chloride, previously reported, has been further derivatized with cyclohexylamine. The amide, m. 120.5-121.5°, has not been analyzed. Ethyl neopentylmethanesulfonate, prepared by reacting the silver salt of the corresponding acid with ethyl iodide, is analytically acceptable whereas that derived from the acid with diazoethane was not. Its properties, b. 87-89°/ 1 mm., n_D^{25} 1.4337, d_4^{25} 1.0276, M_D 49.2 (calc'd 49.0) are somewhat different from those when diazoethane was used (5).

Camphane-10-sulfonyl chloride, m. 84-85°, prepared from the sulfonic acid salt resulting from a Wolff-Kishner reduction of dl-camphor-10-sulfonic acid, was characterized by conversion to the N-benzyl sulfonamide, m. 114-115°, the sulfonmorpholide, m. 193-194°, and the ethyl sulfonate, m. 66-68°. The last named was prepared by the silver salt route. All of these compounds were analytically acceptable. Although the sulfonyl chloride of dl-camphor-10-sulfonic acid melts at nearly the same temperature (81-82°) as does its deketonated analog the melting point of a mixture of the sulfonyl chlorides is significantly lower. While dl-camphor-10-sulfonic acid melts at 202°, the crude deketonated acid is a liquid at room temperature. The morpholide from dl-camphor-10-sulfonic acid melts significantly lower (137-140°) than that from the reduced acid (193-194°).

The Diels-Alder adduct of 9,10-dichloroanthracene and indene, m. 166°, has not been analyzed.

Calibration of the refractometer used in determinations reported in the 1952 annual report (pp. 16-17) was found to be in error. All refractive index values in that report are 0.0009 low.

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Contribution from the Chemical Laboratories
at the Universities of Virginia and Alabama

A STUDY OF ALIPHATIC SULFONYL COMPOUNDS. I. OCTANE-1- and -2-SULFONYL CHLORIDES[1]

By Robert B. Scott, Jr.[2] and Robert E. Lutz[3]

Some time ago Goubau (1) found that the solvolysis of aromatic sulfonyl chlorides is essentially first order when carried out in a large excess of alcohol at 0° to 50°. Recent investigations by Tommila (2) indicate that the reaction takes place by a bimolecular (S_N2) mechanism. Except for Goubau's reference to some unpublished work with phenylmethanesulfonyl chloride and its p-nitro derivative kinetic studies of aliphatic sulfonyl halides have not heretofore been reported.

Since alcoholysis of aliphatic sulfonyl chlorides very probably also proceeds in a bimolecular manner, the mechanisms of reactions of aliphatic sulfonyl halides should be comparable to those of primary alkyl halides and thus subject to steric and polar influences which affect primary alkyl halides. An investigation of the effects of substituent groups on the rates of alcoholysis in boiling ethanol therefore was undertaken.

This report, which is concerned with data obtained for octane-1- and -2-sulfonyl chlorides, represents the first of a series of studies on the magnitude of steric and polar influences on reactions of aliphatic sulfonyl compounds.

New preparations of these known sulfonyl chlorides of octane and determinations of their physical properties are described herein because previous investigators (3,4) did not report density determinations and referred to slight decomposition taking place during distillation.

Octane-1-sulfonyl chloride was prepared by oxidative chlorination of the corresponding mercaptan according to Ziegler (3), by sulfonylation of n-octylmagnesium chloride with excess ethereal sulfuryl chloride according to Cherbuliez (5) and by heating the mercaptan-derived sulfonic acid with either phosphorus pentachloride or thionyl chloride. The products from these three routes had identical physical properties (m. p. 15.5–16.5°, b. p. 94°/ 1 mm., n_D^{20} 1.4591, n_D^{25} 1.4570, d_4^{25} 1.0817, M_D 53.56) and yielded the same amide. No decomposition occurred during distillation when crystals of potassium carbonate were used as boiling stones. The refractive index is in agreement with that reported in the literature (3).

Octane-2-sulfonyl chloride was prepared by sulfonylation of 2-octylmagnesium chloride (5). Distillation under vacuum without decomposition was made possible by potassium carbonate

stabilization of the distilland and by using an unpacked distillation column (b. p. 90°/ 1 mm., n_D^{25} 1.4599, d_4^{25} 1.0834, M_D 53.77, mobile liquid at about -70°). The literature value for the refractive index (4) is substantially the same.

Discussion

Potassium carbonate stabilizes these sulfonyl chlorides (and their ethyl esters) against decomposition during reduced pressure distillation but it is necessary to use an unpacked column such as a Vigreaux and probably partial condensation reflux is preferred to total. Whitmore (6) observed that t-alkyl chlorides can similarly be stabilized against autocatalytic decomposition and Gilman (7) found that sulfonic esters reported to be thermally unstable can be distilled without decomposition after drying with potassium carbonate. Rossander (8) also reported having used this for drying esters of sulfonic acids. This stabilization helps justify the analogy of aliphatic sulfonyl halides to alkyl halides, just as an analogy is quite commonly drawn between alkyl sulfates or sulfonates and alkyl halides.

In determining the rate of ethanolysis of these sulfonyl chlorides a relatively large volume of ethanol was used to reduce the kinetics to first order. As hydrogen halide is a product of alcoholysis of a sulfonyl halide, ethanolic hydrogen chloride was used in order to minimize any effects on rates of attack on sulfonyl chloride or sulfonic ester caused by variations in its concentration[4]. In parts A and B of Table I are shown the amounts of sulfonyl chloride, sulfonic ester and sulfonic acid present at different times during alcoholysis of these sulfonyl chlorides with boiling ethanolic hydrogen chloride. Graphic representations of these data in Figures 1 and 2 illustrate the first order attack on sulfonyl chloride and consecutive conversion of the resultant sulfonic ester into sulfonic acid.

Only differences in steric requirements of the two sulfonyl chlorides can satisfactorily account for the significantly greater rate of ethanolysis determined for octane-1-sulfonyl chloride ($k = 0.089$ mins.$^{-1}$) than that found for octane-2-sulfonyl chloride ($k = 0.014$ mins.$^{-1}$) and the assumption that the alcoholysis of aliphatic sulfonyl halides proceeds by a mechanism similar to that for primary alkyl halides seems well justified. The relative rates of 6.4 to 1 is about what would be expected on the basis of the relative rates of S_N2 reaction of similarly hindered alkyl bromides with potassium iodide in acetone (9), assuming that the sulfo group is the equivalent of a methylene group except about a third larger[5].

Apparently uncatalyzed alcoholysis to produce sulfonic esters is less practicable for sulfonyl halides having large steric requirements than for straight chain ones, Figure 2

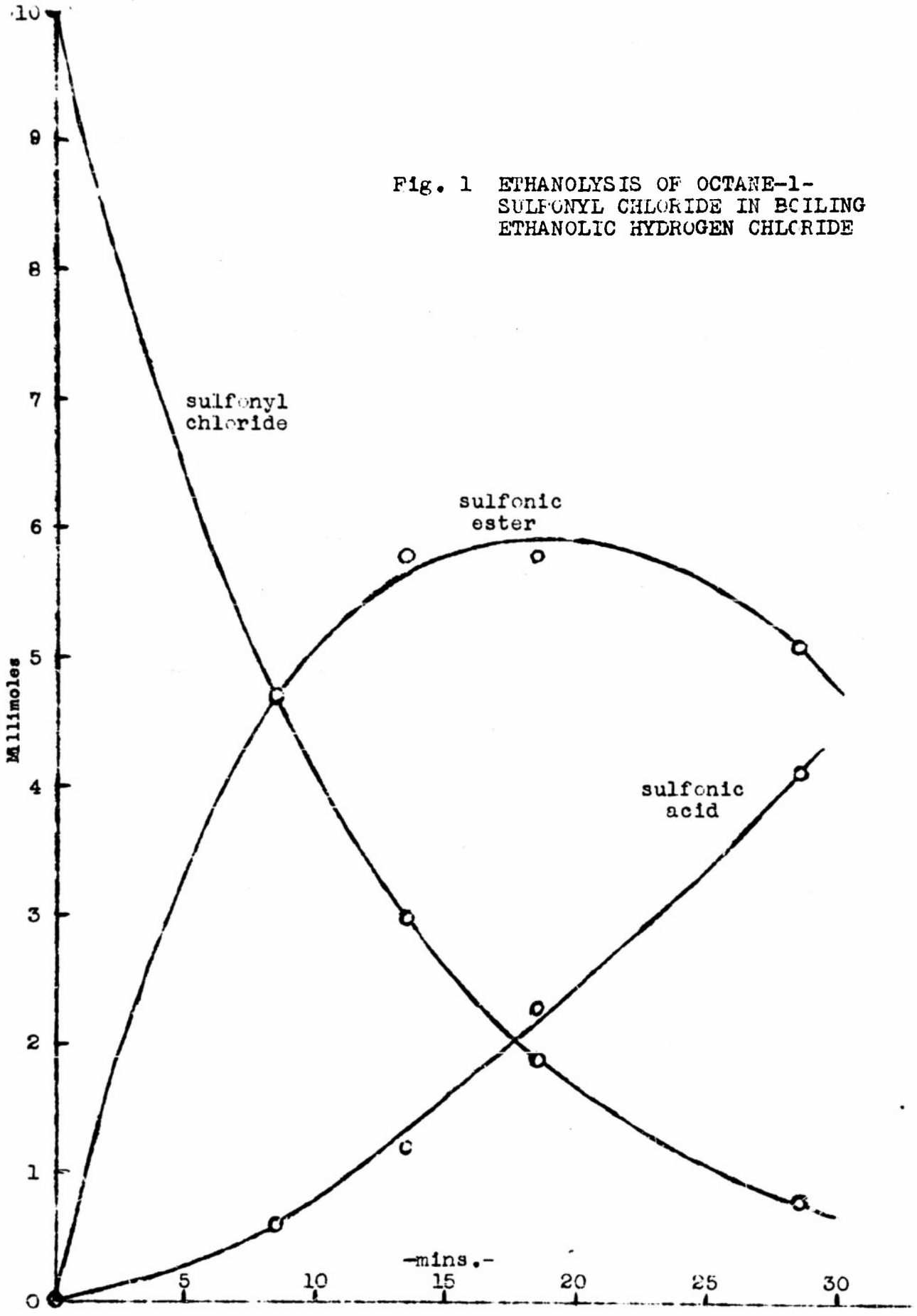

Fig. 1 ETHANOLYSIS OF OCTANE-1-SULFONYL CHLORIDE IN BOILING ETHANOLIC HYDROGEN CHLORIDE

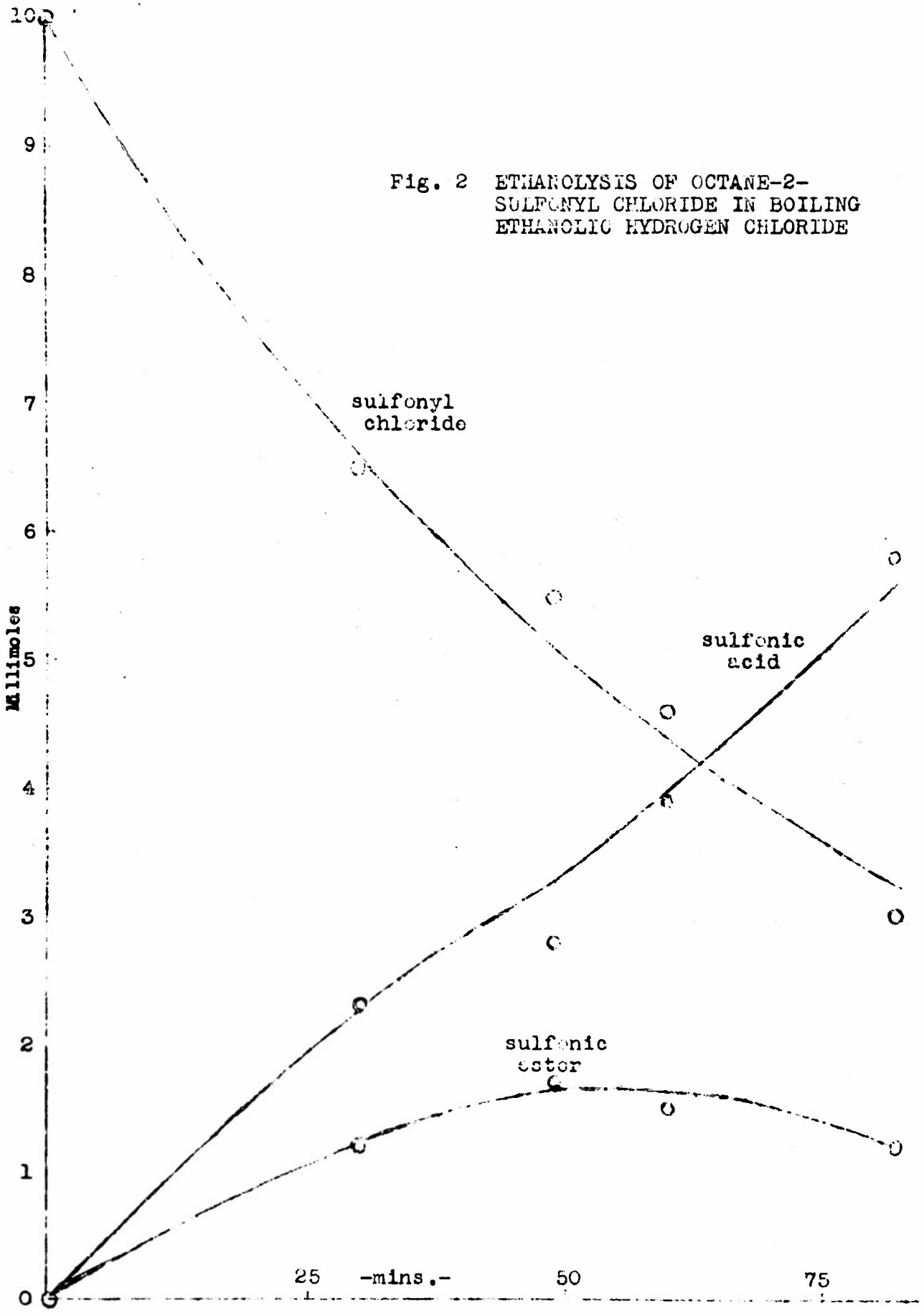

Fig. 2 ETHANOLYSIS OF OCTANE-2-SULFONYL CHLORIDE IN BOILING ETHANOLIC HYDROGEN CHLORIDE

demonstrating that the secondary sulfonic ester is more rapidly attacked than its sulfonyl chloride while Figure 1 shows that the primary one is less rapidly attacked than its sulfonyl chloride.

Although rate constants calculated for the consecutive attack on the sulfonic esters are too erratic to be more than qualitative (see parts A and B of Table I) they are of the same order as the more accurate constants resulting from data (see parts C and D of Table I) obtained when the pure sulfonic esters were reacted with boiling ethanolic hydrogen chloride. The amount of hydrogen chloride necessarily varies during ethanolysis of sulfonyl chlorides consequently the maximum amount that could be present was used in determining the rate of attack on the pure esters. Therefore the resulting constants represent the maximum rates for the consecutive reaction during ethanolysis of the sulfonyl chloride.

In Figure 3 the rates of attack on the sulfonic esters is graphically compared with that for the sulfonyl chlorides. The primary sulfonic ester reacts ($k = 0.051$ mins.$^{-1}$) about 1.2 times as fast as the secondary one ($k = 0.041$ mins.$^{-1}$), thereby indicating that the steric requirements of the latter are significantly greater. Although these esters alkylate the solvent as well as react with the hydrogen chloride, the reaction with boiling ethanol alone is only about 7% as fast as with the alcoholic hydrogen chloride. Again the steric requirements of the secondary sulfonic ester ($k = 0.003$ mins.$^{-1}$) are greater than those of the primary one ($k = 0.004$ mins.$^{-1}$).

Since bases increase the rate of alcoholysis of sulfonyl halides the ~~ethoxide catalyzed~~ ethanolysis of the sulfonyl chlorides was carried out at 25°. Even so the reaction is so rapid that no sulfonyl chloride remains in either case after three minutes while the resultant esters then are more slowly attacked, thus supporting Hirsjärvi's conclusion (10) that shorter than conventional reaction periods would be better for preparing sulfonic esters in this manner. As a ~~four- to five-~~ three-fold excess of ethoxide was present after the sulfonyl chlorides had been reacted the base attack on the resultant esters can be considered to be partially reduced toward first order for comparative purposes. At least these rough values ($k_1 = 0.004$ mins.$^{-1}$, $k_2 = 14 \times 10^{-2}$ moles^{-1} mins.$^{-1}$ for the primary and $k_1 = 0.008$ mins.$^{-1}$, $k_2 = \_\_ \times 10^{-\_}$ moles^{-1} mins.$^{-1}$ for the secondary) serve to fix the order of magnitude and to indicate that base attack is much more prominent at this temperature than is solvolysis (see parts E and F of Table I).

As further evidence of the greater steric requirements of the secondary sulfonyl chloride, saponification with hot aqueous potassium carbonate solution proceeds roughly eight times as fast with the primary as with the secondary sulfonyl chloride.

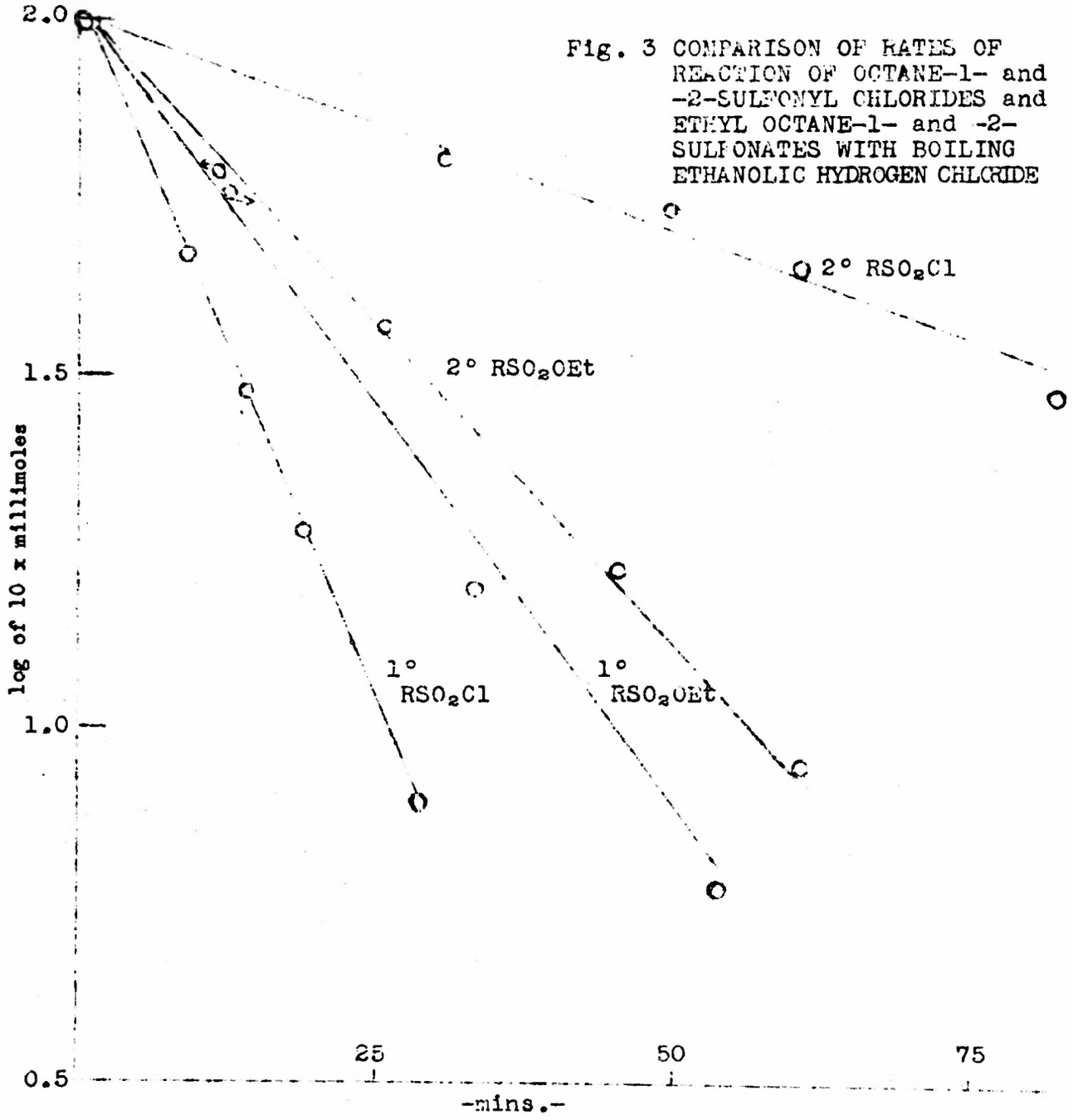

Fig. 3 COMPARISON OF RATES OF REACTION OF OCTANE-1- and -2-SULFONYL CHLORIDES and ETHYL OCTANE-1- and -2-SULFONATES WITH BOILING ETHANOLIC HYDROGEN CHLORIDE

TABLE I

ATTACK ON OCTANESULFONYL COMPOUNDS BY ETHANOL, BY HYDROGEN CHLORIDE AND BY SODIUM ETHOXIDE

Experiment[a]	Time mins.	RSO_2Cl Mg.moles	RSO_2OEt Mg.moles	RSO_2OH Mg.moles Obt'd	RSO_2OH Mg.moles Calc'd	k_1 $mins.^{-1}$	k_2 $mins.^{-1}$
A	8.5[b]	4.7	4.7	0.3	0.6	0.090	
	13.5[b]	3.0	5.8	1.1	1.2	0.089	0.01[c]
	18.5[b]	1.9	5.8	2.2	2.3	0.090	0.03[c]
	28.5[b]	0.8	5.1	4.1	4.1	0.089	0.04[c]
					Average[d]	0.089	
B	30	6.5	1.2	0.4	2.3	0.014	
	49	5.5	1.7	0.9	2.8	0.012	0.04[c]
	60	4.6	1.5	0.9	3.9	0.013	0.05[c]
	82	3.0	1.2	3.0	5.8	0.015	0.06[c]
					Average[d]	0.014	
C	11		6.2	3.0	3.8	0.043	
	33		1.6	7.3	8.4	0.056	
	53.5		0.6	8.9	9.4	0.053	
					Average[d]	0.051	
D	12		5.7	2.6	4.3	0.047	
	25		3.7	4.3	6.3	0.040	
	45		1.7	6.7	8.3	0.039	
	60.5		0.9	7.0	9.1	0.040	
					Average[d]	0.041	
E	3	0.0	5.3		4.7	>1.	
	10	0.0	5.2		4.8		0.004[e]
	50	0.0	4.4		3.6		
F	3	0.0	8.2		1.8	>1.	
	14	0.0	7.5		2.5		0.008[f]

A- Ethanolysis of Octane-1-sulfonyl Chloride. Mixture of 2.13 g. of sulfonyl chloride, 0.50 g. of hydrogen chloride and 11.2 g. of dry ethanol refluxed different times and analyzed.

B- Ethanolysis of Octane-2-sulfonyl Chloride. Treated as A.

C- Alkylation of Hydrogen Chloride with Ethyl Octane-1-sulfonate in Ethanol. Mixture of 2.22 g. of ethyl sulfonate, 0.83 g. of HCl and 11.0 g. of dry ethanol refluxed and analyzed.

D- Alkylation of Hydrogen Chloride with Ethyl Octane-2-sulfonate in Ethanol. Treated as C.

E- Alkaline Ethanolysis of Octane-1-sulfonyl Chloride. Mixture of 1.0 g. of sodium in 50 cc. of dry ethanol reacted with 2.13 g. of sulfonyl chloride at 20-25° and analyzed.

F- Alkaline Ethanolysis of Octane-2-sulfonyl Chloride. Treated as E.

The only derivative previously reported for octane-1-sulfonic acid is the phenylhydrazine salt (11). Accordingly several characterizing derivatives were prepared (see Table II) in the conventional manner except for the sulfonphthalimide. This compound (m. p. 120.5-122°) which could not be made by reacting the sulfonyl chloride with phthalimide or its salt, presumably because of the large steric requirements of the base, is the acylation product of the sulfonamide and phthalyl chloride by a modification of the method of Evans (12) in which the higher reaction temperature was attained by the omission of a solvent. No solid derivative of octane-2-sulfonic acid has been disclosed in the literature. The sulfonphthalimide (m. p. 95.5-96.5°), prepared from the crude liquid sulfonamide, was the only solid derivative obtainable for this system.

Although the ethyl sulfonates can be prepared directly from these sulfonyl chlorides in the presence of cold pyridine (13) a more satisfactory synthesis is the essentially quantitative reaction of the sulfonic acids with excess ethereal diazoethane analogous to the preparation of methyl sulfonates using diazomethane (14). Like the sulfonyl chlorides, these esters can be distilled under reduced pressure in the presence of potassium carbonate without decomposition.

* *

Footnote to Table I

[a] Each experiment based on 10.0 mg.moles starting sulfo cmpd.

[b] Actual time measured was 1.5 mins. longer in each case. The following consts. were obt'd based on time other than zero: 0.090 (10 & 15 mins.), 0.092 (15 & 20 mins.), 0.086 (20 & 30 mins.), 0.091 (10 & 20 mins.), 0.089 (10 & 30 mins.), 0.088 (15 & 30 mins.); mean value of 0.089 was used then for calculation of time zero. With 1.5 mins. deducted from observed times all points including calculated time zero fall on a straight line in a log conc. vs time plot. Accuracy of data may not warrant such correction, however, the mean rate constant calculated from observed time (k=0.082 mins.$^{-1}$) also significantly differs from that of the secondary sulfonyl chloride.

[c] Calc'd from $B = (k_1 A_0 / k_2 - k_1)(e^{-k_1 t} - e^{-k_2 t})$ in which B = conc. of ester at time t; k_1 = rate const. for disappearing RSO_2Cl; A_0 = init. conc. RSO_2Cl; k_2 = rate const. for disappearing ester.

[d] Average values determined graphically.

[e] Assuming 1st order and calculations based on data for 3 & 50 mins. or for 10 and 50 mins. Second order constant similarly determined is 0.00014 moles^{-1} mins.$^{-1}$.

[f] Assuming first order and calculations based on data for 3 and 14 mins. Second order constant similarly determined is 0.00026 moles^{-1} mins.$^{-1}$.

* *

TABLE II

AMIDE DERIVATIVES OF OCTANE-1-SULFONIC ACID

Derivative	m.p.	Analyses (%)					
		Calculated			Found		
		C	H	N	C	H	N
Dimethylamide[a]	23.5–24.5			6.33			5.63
Piperidide	33–34			5.36			5.28
Dibenzylamide	35.5–36.5	70.73	8.37		70.46	8.42	
Anilide	41.5–42.5			5.20			5.37
Morpholide	47–48			5.32			5.23
Methylamide	47.5–48	52.13	10.21		52.00	10.06	
p-Toluidide	54.5–55.5			4.94			4.94
Cyclohexylamide	63.5–64.5			5.09			5.30
p-Chloroanilide	64–65			4.61			4.48
Amide	70.5–71.5	49.71	9.91	7.25	49.70	9.90	7.29
Benzylanilide	74–75	70.15	8.13		69.90	8.18	
B-Naphthylamide	75.5–76.5			4.38			4.45
Benzylamide	77.5–79	63.56	8.88		63.82	8.70	
n-Octylamide	87.5–88.5			4.59			4.47
p-Nitroanilide	92.5–94			8.91			9.17
Phenylhydrazide	126–127.5	Decomposed before analysis					

[a] Not analytically pure.

Experimental

Ethanolysis of the Sulfonyl Chlorides - A mixture of 2.13 g. (0.0100 mole) of the particular sulfonyl chloride, 0.50 g. (0.014 mole) of hydrogen chloride and 11.2 g. (0.24 mole) of dry ethanol was refluxed. Weighed aliquots were periodically removed and quenched in cold water. The composition of the mixture of sulfonyl chloride and sulfonic ester remaining after aqueous extraction of the sulfonic acid was estimated from the weight of the mixture and its refractive index after total distillation in a small electrically heated static type molecular still (5–10 mm. distillation path, 0.02–0.05 mm pressure) equipped with a U-shaped condenser instead of the conventional cold-finger in order to increase the rate of distillation. Temperatures in excess of 50° were avoided and the material balance of the distillations was good. The aqueous extract containing sulfonic acid was concentrated and treated with barium chloride solution. The amount of sulfonic acid in the alcoholysis mass then was calculated from the weight of dried (75° in vacuo) barium sulfonate precipitated. It also was calculated by stoichiometric difference from the amounts of sulfonyl chloride and ester. The material balance was good in the case of the primary sulfonyl chloride but only fair in the case of the secondary one because of the appreciable solubility of its barium sulfonate. The results are recorded in parts A and B of Table I.

Ethyl octane-1-sulfonate was prepared in 62% conversions by ethanolysis of the sulfonyl chloride in the presence of cold pyridine and in essentially quantitative yield by distilling ethereal diazoethane into an ether solution of the sulfonic acid and was distilled through a 36 cm. x 16 mm. Vigreaux column fitted with a partial condensation still head. In order to avoid possible decomposition during the reduced pressure distillation crystals of potassium carbonate were used as boiling stones. Physical characteristics are: B. p. 113°/ 1 mm., n_D^{25} 1.4382, d_4^{25} 1.0009, M_D 58.3.
Anal. Calc'd for $C_{10}H_{22}O_3S$: C, 54.02; H, 9.98.
Found: C, 54.00; H, 9.83.

Ethyl octane-2-sulfonate was prepared in analogous manner by reacting the sulfonic acid with diazoethane (b. p. 101°/ 1 mm., n_D^{25} 1.4388, d_4^{25} 1.0029, M_D 58.3).
Anal. Calc'd for $C_{10}H_{22}O_3S$: C, 54.02; H, 9.98.
Found: C, 54.03; H, 9.76.

Action of Alcoholic Hydrogen Chloride on the Sulfonic Esters- Rates of attack on the intermediate ethyl esters by ethanolic hydrogen chloride were determined in a manner somewhat like that described for ethanolysis of the sulfonyl chlorides. A mixture of 2.22 g. (0.0100 mole) of the ethyl octanesulfonate, 0.83 g. (0.023 mole) of hydrogen chloride and 11.0 g.

(0.24 mole) of dry ethanol was refluxed. Periodically weighed aliquots were removed and treated as for ethanolysis of the sulfonyl chlorides except that the absence of sulfonyl chloride obviated distillation of recovered ester. The results are recorded in parts C and D of Table I.

Solvolysis of the Sulfonic Esters - Rates of attack by the solvent were estimated by refluxing a mixture of 1.11 g. (0.0050 mole) of ethyl ester in 20 cc. of ethanol for 9.3 hours. After aqueous extraction of the sulfonic acid produced, 0.51 g. (0.0005 mole) of the primary sulfonic ester and 0.20 g. (0.0009 mole) of the secondary were recovered, thus indicating that solvolysis had proceeded 90% ($k = 0.004$ mins.$^{-1}$) and 82% ($k = 0.003$ mins.$^{-1}$) respectively.

Saponification of the Sulfonyl Chlorides - To 0.21 g. (1.0 mg.mole) of sulfonyl chloride in a covered 10-cc. beaker was added 0.15 g. (1.1 mg.moles) of potassium carbonate as a 10% aqueous solution. After the mixture had been heated momentarily to boiling, the covered beaker was placed on a steam bath which maintained the reaction mass at about 75°. After approximately an hour the primary sulfonyl chloride had been completely saponified as judged by its disappearance as a separate phase. A trace of the secondary remained as a separate phase after about eight hours.

Alkaline Ethanolysis of the Sulfonyl Chlorides - The sulfonyl chloride (2.13 g., 0.0100 mole), followed by a 10-cc. ethanol rinse, was added rapidly to a stirred solution of 1.0 g. (0.043 g.atom) of sodium in 40 cc. of dry ethanol at 19°. Aliquots were periodically removed from the charge, which was maintained at 20-25° by cooling, and analyzed for sulfonyl chloride and ester in the manner described under the earlier section on ethanolysis of the sulfonyl chlorides. The sulfonyl chloride which had reacted also was determined by mercuric nitrate titration of the chloride ion produced. The amount of sulfonic acid was estimated by stoichiometric difference. The results are shown in parts E and F of Table I.

Solid Derivatives from the Sulfonyl Chlorides - Numerous sulfonamides were prepared in the conventional manner from octane-1-sulfonyl chloride, heating the amine-sulfonyl chloride mixture with pyridine as a catalyst being necessary in the case of aromatic amines while aliphatic amines react quite vigorously in ether solution. "Iso-octane" (2,2,4-trimethylpentane) is a most satisfactory solvent for recrystallization of the amides. In Table II are shown the various derivatives prepared.

Preparation of a solid derivative from octane-2-sulfonyl chloride was difficult. Neither the amide, the benzyl-

anide, nor the p-chloroanilide could be induced to crystallize. The sulfonyl chloride did not react when heated with potassium phthalimide. The method of formation of the sulfonphthalimide recommended by Evans (12), wherein the sulfonamide is reacted with phthalyl chloride in boiling toluene, failed to force a reaction. However, when an equimolar mixture of the crude liquid sulfonamide (0.82 g., 0.0042 mole) and phthalyl chloride (symmetrical) (0.86 g.) was heated hydrogen chloride began to evolve at 130–140°. Heat was increased until no more gas was given off at 225°. After the residue had been dissolved in benzene and clarified with charcoal, the sulfonphthalimide was repeatedly crystallized from "isooctane" containing 5% (by volume) benzene or 8% chloroform until there was no increase in melting point (95.5–96.5°). The yield of such recrystallized product was only 9% (0.12 g., 0.0004 mole).

Anal. Calc'd for $C_{16}H_{21}O_4NS$: C, 59.42; H, 6.55.
Found: C, 59.47; H, 6.13.

Like the secondary sulfonyl chloride, the primary would not react with potassium phthalimide, nor would it react with phthalimide alone. The sulfonphthalimide was prepared from the primary sulfonamide (0.70 g., 0.0036 mole) by heating with an equimolar quantity of symmetrical phthalyl chloride (0.73 g.) as in the case of the secondary except that hydrogen chloride did not commence to be evolved until the charge had been heated to 175°. A 60% yield (0.69 g., 0.0021 mole) of analytically pure sulfonphthalimide (m. p. 120.5–122°) was obtained.

Anal. Calc'd for $C_{16}H_{21}O_4NS$: C, 59.42; H, 6.55.
Found: C, 59.33; H, 6.61.

Summary

Octane-1- and -2-sulfonyl chlorides and the ethyl esters of the corresponding sulfonic acids can be distilled *in vacuo* without decomposition through an unpacked column provided the distilland is stabilized with potassium carbonate.

Useful physical constants have been determined for octane-1- and -2-sulfonyl chlorides and for the ethyl esters of the corresponding sulfonic acids.

A number of solid derivatives of octane-1-sulfonyl chloride and one solid derivative of octane-2-sulfonyl chloride have been prepared.

Steric hindrance to ethanolysis by octane-2-sulfonyl chloride has been demonstrated.

Footnotes

1 Principally from the 1949 dissertation presented by Robert F. Scott, Jr. in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Virginia. A minor part of this work was completed at the University of Alabama as a contribution to project NR 055 222 under contract N9 onr 96100 with the Office of Naval Research. Rights reserved for reproduction in whole or in part for any purpose of the United States Government.

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3 Cobb Chemical Laboratory, University of Virginia, Charlottesville, Va.

4 Goubau (1) considered an apparent drift from first order ethanolysis of aromatic sulfonyl chlorides was due to autocatalysis from hydrogen chloride. If allowance is made for an increase in the total acidity on which he based his calculations due to slow solvolytic attack on the sulfonic ester (concurrent with the more rapid attack by hydrogen chloride which results in no change in total acidity) the apparent drift disappears. Although Goubau observed an increased rate of ethanolysis when alcoholic hydrogen chloride was used this would not be expected to affect a comparison of isomeric sulfonyl chlorides. Recent work with another aliphatic sulfonyl chloride by John B. Gayle at the University of Alabama indicates that there is no change in rate occassioned by the added hydrogen chloride.

5 Since n-butyl bromide is attacked by potassium iodide in acetone sixteen times as fast as B-methylbutyl bromide, the primary sulfonyl chloride would react $16(0.77/1.04)^3 = 6.5$ times as fast as the secondary one assuming that the hindrance varies inversely as the surface exposed of the attacked atoms.

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MECHANISM OF RETROPINACOL-TYPE REARRANGEMENTS[1]

ROBERT B. SCOTT, JR., AND JOHN B. GAYLE

Received January 2, 1953

The consensus of modern theories of rearrangement is that strained carbonium ions derived from carbinols, halides, olefins, etc., rearrange spontaneously when less-strained intermediates are formed by migration of alkyl or aryl groups (1). Such views do not account for the fact that considerably greater proportions of rearranged products are obtained from strained carbinols than from the corresponding olefins even though the same carbonium ion is considered to be involved during replacement of the hydroxyl group of a particular carbinol and addition of a hydrogen halide to the corresponding olefin. Likewise, these views fail to account for the fact that different hydrogen halides give different proportions of rearranged products when added to the same olefin. Thus, pinacolyl alcohol gives almost exclusively rearrangement products with hydrogen chloride (2), whereas *tert*-butylethylene gives about 60% rearrangement products with hydrogen chloride and 10% with hydrogen iodide (3).

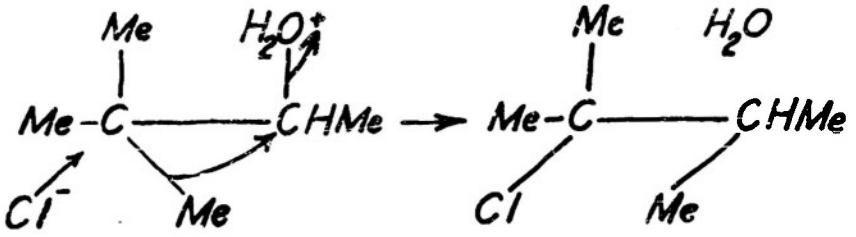


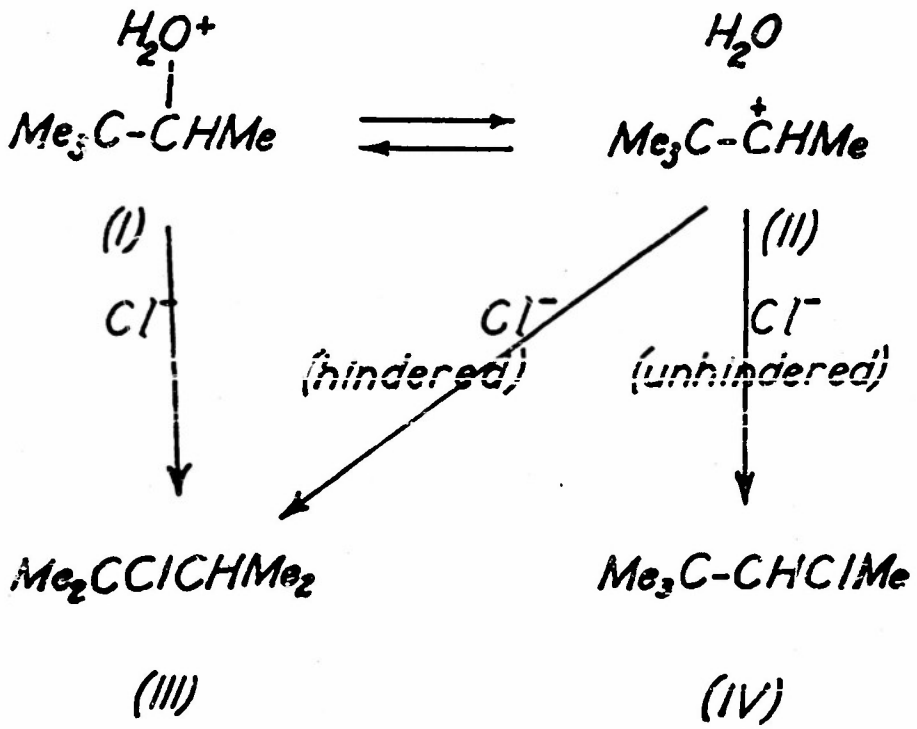
FIG. 1

When the common view-point is modified, however, to consider that, first, a carbonium ion does not rearrange *per se* but may be rearranged by base attack, and second, an oxonium ion can be rearranged in similar manner, many apparent anomalies become logical. In spite of the fact that Winstein has inferred such a mechanism (4) from the work of Bartlett (5), no one has followed this reasoning to the logical explanation of apparently anomalous results as is done in the following descriptions of probable reaction mechanisms for the cases cited above.

When pinacolyl alcohol is reacted with hydrogen chloride, an oxonium ion is formed. Some of this loses water to give an equilibrium mixture of oxonium (I) and carbonium (II) ions. That remaining as oxonium ion is converted almost exclusively to rearrangement products because normal S_N2 attack is too hindered to be significant. Instead of attacking the oxonium carbon atom, the

[1] From a part of the research of John B. Gayle to be incorporated into his dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Carried out as part of project NR 055 222 under contract N9onr 96100 between the Office of Naval Research and the University of Alabama. Rights reserved for reproduction in whole or in part for any purpose of the United States Government.

chloride ion attacks, by default, the *beta*, or neo, carbon atom and displaces a methyl carbanion. This readily attacks the back face of the oxonium carbon atom to give a rearranged product (III) because there is no hindrance to such attack. (See Figure 1.) The carbonium ion portion of the equilibrium mixture gives rise to the same proportions of rearrangement products as does *tert*-butylethylene, for the carbonium ion probably is the only intermediate involved when a hydrogen halide is added to the latter. In this instance, a considerable amount of unrearranged product (IV) results from simple neutralization of the carbonium ion, thereby demonstrating that the base is not necessarily hindered from



attacking the carbonium carbon atom. However, an attacking base which is so located that it is hindered from such a reaction may neutralize the carbonium ion indirectly by means of a methyl carbanion which it displaces by attacking the *beta*, or neo, carbon atom, thereby yielding a rearranged product. Thus the difference in amounts of rearranged product from pinacolyl alcohol and from *tert*-butylethylene may now be explained on a fundamental basis. Carbinols form mixtures of oxonium ions and carbonium ions. The oxonium ions may be highly hindered from normal attack and lead to rearranged products. The carbonium ions are relatively unhindered and consequently lead to greater amounts of normal products. Because olefins form only carbonium ions, smaller amounts of rearranged products are to be expected. Since a smaller base will have greater access to the neo carbon atom, it is not surprising that hydrogen chloride adds to *tert*-butylethylene with formation of more rearrangement products than does hydrogen iodide, for the chloride ion is considerably smaller than the iodide ion.

The accessibility of the *beta* carbon atom is an important factor in accounting for many apparent anomalies. Viewing the mechanism of the retropinacol-type rearrangement as involving a base attack at the *beta* carbon atom, it follows that hindrance to such attack will result in reaction taking place to a greater extent through the carbonium ion intermediate, thereby forming less rearrangement products. This hindrance may be of two types:

(a) The result of bulky substituents which shield the *beta* carbon atom and/or the result of a bulky attacking base, and

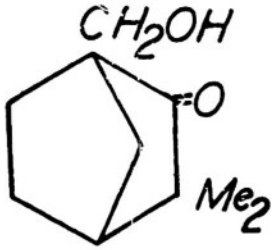
(b) The result of electrostatic repulsion by electron-dense substituents located in a position to shield the *beta* carbon atom from a rearranging base attack. In this type the electron density of the base also is significant.

Hindrance to base attack at the *beta* carbon atom accounts for many cases frequently pointed out as anomalous. For example, Wheland considers the rearrangement of carbonium ions *per se* as being a completely successful view in that it permits correlation of a large number of facts and does not appear to be in direct conflict with known facts "although it may perhaps occasionally lead one to expect the formation of a rearranged product which is not actually obtained (sic)" (6). Likewise, Whitmore points out the "radical difference" between pentaglycol, $Me_2C(CH_2OH)_2$, and neopentyl alcohol in that the former is not rearranged by hydrogen bromide (7). Other cases in which rearranged products might be expected but are not actually obtained are discussed below. For instance, 10-hydroxytenchone (V) is not rearranged on treatment with phosphorus pentachloride (8) because the *beta* carbon atom is located at a cage-head of a bicyclo (2.2.1) system, and, therefore, is protected from base attack. Less obvious is the hindrance afforded by the distorted methylene bridge and its substituents when 3-hydroxymethylcamphane (VI) is dehydrated without rearrangement by syrupy phosphoric acid (9), whereas dehydration of cycloheptyl carbinol with oxalic acid or zinc chloride leads to rearrangement (10). With the commonly accepted views of cationic rearrangements, the strained bicyclic compound would be expected to lead to more rearrangement products than the relatively strainless monocyclic one. Conversion of 8-hydroxycamphane (VII) (11) and tricyclol (VIII) (12) into the corresponding chlorides by phosphorus pentachloride also take place without the formation of rearranged products. Likewise, 2,10-dichlorocamphane (IX) yields the unrearranged dihydroxy compound with silver oxide in boiling dilute alcohol (13) and the corresponding dibromide yields 10-bromo-2-camphanol with silver hydroxide in aqueous acetone (14). Similarly, thionyl chloride converts 3-hydroxymethylcamphor (X) into 3-chloromethylcamphor (14).

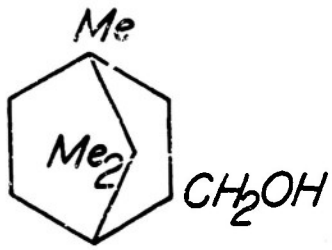
Besides pentaglycol, the following show non-rearrangement, probably because of the high electron density of the neo carbon atom substituents: Pentaerythritol on reaction with hydrogen bromide and the resultant bromide on conversion to the original poly-alcohol (15); pentaglycerol, $MeC(CH_2OH)_3$, on conversion to the tribromide (16); and γ-1-piperidylneopentyl alcohol on conversion to the corresponding chloride with thionyl chloride (17). Of course, the larger bulk of the substituted groups helps somewhat to shield the neo carbon atom.

The literature is replete with further data supporting this view of the retro-

pinacol-type rearrangements. The examples cited, however, seem adequate to establish the validity of the proposed mechanism. The utility of this mechanism is evident from the foregoing discussion of probable reaction mechanisms.



(V)



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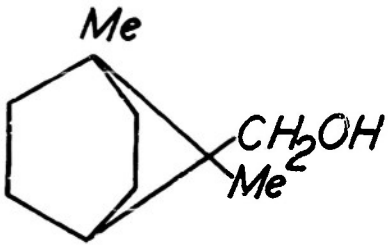

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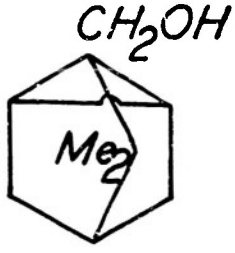

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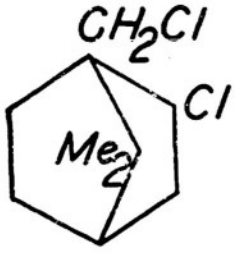

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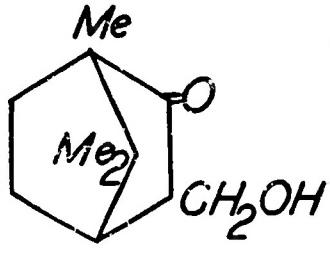

(X)

In conclusion, it appears that:

1. The rearrangement of carbonium ions *per se* is not a completely successful view of retropinacol-type rearrangements. With such views rearranged products are expected in many cases in which they are not obtained. Nor do such views have quantitative value.

2. Considering retropinacol-type rearrangements to be the result of an attack by a secondary base (carbanion) displaced by S_N2 base attack at the *beta*

carbon atom not only accounts for all cases of such rearrangement but also accounts for those cases in which rearrangement fails to take place. Further, this view has more than qualitative value in accounting for varying proportions of rearranged products under different conditions.

3. Shielding the *beta* carbon atom, either by bulky groups or by electron-dense neighbors, hinders base attack at that carbon and, hence, hinders rearrangement.

SUMMARY

Contrary to current views, strained cations do not rearrange *per se* but are rearranged by base attack at the *beta* carbon atom. Oxonium ions form little unrearranged products from the normal S_N2 attack when the base is sterically hindered; instead, an unhindered carbanion attacks when it is displaced by base attack at the *beta* carbon atom. Normal and rearranging base attacks may likewise occur with carbonium ions with the great difference that the carbonium carbon atom is relatively unhindered and greater proportions of normal products are obtained. Access of the *beta* carbon atom to base attack and, probably, strength of the base determine the proportion of rearrangement products. Rearrangement can be prevented by shielding the *beta* carbon atom by either bulky or electron-dense groups. Size and electron density of attacking base must be considered conjointly with shielding groups. Many "anomalous" cases of failure of the retropinacol-type rearrangement to occur are shown to result from protection of the *beta* carbon atom.

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